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The O_2^+ - C_2D_2 Reaction: An Endoergic Stripping Process

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ABSTRACT

We have determined the product velocity vector distributions for the endoergic (ΔE_o^o = 2.23eV) atom abstraction reaction O_2^+ (C_2D_2,C_2D) O_2D^+ at a number of values of the initial relative energy. Deuterium atom abstraction occurs at higher energies by a spectator stripping process. An energy threshold for the zero angle reactive scattering process is observed when the energy of the O_2^+ projectile relative to the abstracted atom is equal to the endoergicity of the reaction. The results show that the spectator stripping process is not to be uniquely associated with exoergic reactions or those which proceed along monotonically decreasing potential energy surfaces.

In ion-molecule collision phenomena, the spectator stripping model has proved to be a useful first approximation to the dynamics of exoergic hydrogen, and deuterium atom abstraction reactions[1] such as $N_2^+(H_2,H)\ N_2H^+$, $N_2^+(CH_4,CH_3)\ N_2H^+$, $Ar^+(D_2,D)\ ArD^+$, and $CO^+(D_2,D)\ COD^+$. In its simplest, or "ideal" form, the model involves no force and thus no recoil between the departing reaction products. Applied to the $Ar^+(D_2,D)ArD^+$ reaction, for example, the model leads to the prediction of no velocity change for the freed or "spectator" atom as a result of the collision, and the ionic product ArD^+ appearing only at zero angle in the barycentric system, with a speed determined by the conservation of momentum of the projectile-abstracted atom system. The reactions mentioned above do show a high intensity product peak at or very near the velocity predicted by the ideal stripping model over considerable ranges of initial relative energy. There are, of course, other important features[2,3] to the product velocity vector distributions for these abstraction reactions, but the stripping peak is an intriguing common feature.

The spectator stripping model also leads to the prediction that in an atom abstraction reaction, the internal energy U' of the ionic product will be equal to the initial kinetic energy of the projectile ion relative to the abstracted atom E_a, plus the exoergicity of reaction $-\Delta E_o^o$:

$$U' = E_a - \Delta E_o^o$$

It is of course a general physical requirement that U' be equal to or greater than zero. For exoergic reactions this

presents no limitation on the projectile energy, aside from the ever present requirement that U' be small enough to insure product stability. However, for endoergic reactions there is clearly also a lower limit $E_a = \Delta E_o^o$ for the projectile energy below which spectator stripping is not possible. Moreover, the nature of the stripping process suggests intuitively at least the possibility that it might only be operative in exoergic reactions for which the potential energy surface is essentially smoothly decreasing from reactants to products. The purpose of the work reported in this paper was to examine the dynamics of an endoergic atom abstraction reaction to determine whether the stripping phenomenon can occur in such a process, and to attempt to detect the predicted energy threshold for spectator stripping.

The reaction

$$O_2^+ + C_2D_2 \longrightarrow O_2D^+ + C_2D \qquad \Delta E_o^o = 2.23\text{eV}$$

was chosen because it is a simple endoergic[4] atom abstraction reaction with rather favorable kinematic aspects. For a given projectile laboratory energy E_o, the energy relative to the abstracted atom is

$$E_a = E_o M(D)/(M(O_2) + M(D)) = 0.0588E_o$$

whereas the energy of the projectile relative to the whole deuteroacetylene molecule is

$$E_r = E_o M(C_2D_2)/(M(O_2) + M(C_2D_2)) = 0.467E_o$$

For the projectile energies employed in this work, E_r is always well in excess of the 2.23eV endoergicity of the reaction, while E_a may be comparable to or greater than 2.23 eV. Thus if a kinetic energy threshold for production

of O_2D^+ is observed, it is strong evidence that the spectator stripping model is a good first approximation to the dynamics of even this endoergic reaction.

EXPERIMENTAL

The instrument used in this work consists of a magnetic mass spectrometer for preparation of a collimated beam of primary ions of known mass and energy, a scattering cell to contain the target gas, an ion detection train made up of an electrostatic energy analyser, a quadrupole mass spectrometer, and an ion counter. The detector components and the exit aperture of the scattering cell are mounted on a rotatable lid which permits simultaneous angular and energy measurements of the ion products. The major components of the apparatus have been described previously[2]. In all important respects, the constitution and operation of the apparatus and the data acquisition and reduction techniques were the same as we have used in earlier work[2,3].

The primary ions were extracted from a microwave discharge through oxygen[5]. Because of the low electron temperature (~5eV) that is characteristic of these discharges, relatively few electrons have energies greatly in excess of 10eV. Consequently, most of the ionization is produced by electrons which are energies which are not much greater than the ionization energy of the gas (12.2eV), and the number of metastable excited ions such as $O_2^+(^4\pi_u)$, which requires 16eV to be produced, is much smaller in a microwave discharge than in a conventional 50eV electron impact source.

Beam attenuation experiments of the type described by Turner, et al[6], showed that the momentum analyzed O_2^+ beam

contained less than 3% excited metastable ions. The vibrational excitation of the ions in the $^2\pi_g$ ground state of O_2^+ is not known, but Franck-Condon factors[7] suggest that most ions are in the excited vibrational levels 1-5, with the average vibrational energy being approximately 0.3eV.

RESULTS AND DISCUSSION

Figure 1 shows contour maps of the velocity vector distribution of O_2D^+ determined at two projectile energies. A barycentric coordinate system is used, and the product intensity is given as a specific intensity[2] or cartesian flux[8] in arbitrary units. The quantity Q is the difference between the final and initial relative kinetic energies of the products and reactants. The small crosses at or near the intensity peak mark the location of the velocity of O_2D^+ calculated according to the spectator stripping model.

It is clear that most of the product intensity lies in a small range of speed and angle centered at the ideal stripping velocity, having dimensions which are only slightly greater than the primary beam profile. It appears then that virtually all the atom abstraction that occurs at these very high <u>total</u> relative energies takes place by the spectator stripping process. The rapid fall-off of product intensity with increasing scattering angle suggests that the stronger interactions associated with the larger angle scattering in fact lead to such processes as collisional dissociation, excitation, or perhaps more complex reaction processes which compete with the simple atom abstraction process.

The O_2D^+ intensity in the maps of Figure 1 and in the other experiments we performed lies almost entirely in the range $-10 \leqslant Q \leqslant -2.23$. For ground state reactants, and for the products O_2D^+ and C_2D, Q is given by

$$Q = -\Delta E_o^o - U'$$

The product internal excitation U' has a lower limit of zero, and an upper limit of the sum of the dissociation energies of the O_2^+-D and C_2-D bonds. Thus Q must lie in the range[4]

$$-9.7 \leqslant Q \leqslant -2.23$$

The absence of products in regions in which Q is more negative than -10eV suggests that there are no reactions of appreciable importance in which O_2D^+ is formed and C_2D is either electronically excited or fragmented.

Table I gives the ratio of the most probable product laboratory velocity to the projectile velocity. For an ideal stripping process, this ratio should be 32/34 = 0.941, and most of the data are quite close to this value, particularly those experiments at the higher energies. The values of Q at the intensity peaks are also given in Table I. The values are all more negative than -5eV. If all product internal excitation were to appear in the O_2D^+ fragment, the most negative value of Q consistent with the stability of O_2D^+ would be -4.80eV. Since the observed most probable values of Q are as much as 1.3eV more negative than this, we can conclude that the C_2D fragment is produced internally excited by amounts of this general magnitude, even though little or no momentum is

transferred to it in the reaction process. If the abstraction were essentially a Franck-Condon process with respect to the C_2D fragment, internal excitations of this magnitude would appear to be reasonable.

The product intensity contour maps and the scans of intensity at zero scattering angle indicate that the abstraction reaction is well described by the spectator stripping model. One expects on this basis that the differential cross section for abstraction at zero scattering angle should exhibit a threshold at a projectile energy of 2.23eV relative to the abstracted atom, or at 37.9eV in the laboratory system. Figure 2 shows the zero angle differential cross section as a function of projectile energy. The differential cross section $I(\theta = 0)$ is calculated from the specific intensities $\overline{I}$ plotted in the contour maps by the expression

$$I(\theta = 0) = \int_0^\infty \overline{I}(u)\, u^2 du.$$

For projectile energies above 75eV in the laboratory system, the cross section for abstraction falls with increasing projectile energy. This behavior is similar to that observed for several other atom abstractions,[2,3,9] and is primarily a result of the difficulty of stabilizing the ionic reaction product against dissociation as the collisional energy increases. For laboratory energies between 40 and 60eV the cross section falls as the energy <u>decreases</u>, and reaches 0.1 its maximum value at 45eV laboratory energy. Thus the behavior of the cross section at these lower energies seems to be consistent

with a threshold at approximately 38eV in the laboratory system. The total relative energy of O_2^+ and C_2D_2 is 17.7eV at this laboratory energy, far in excess of the reaction endoergicity or any additional energy barriers that might be expected. The projectile energy relative to the abstracted atom is close to 2.23eV at the reaction threshold, as predicted by the stripping model. The fact that threshold behavior is observed even though the total relative energy of O_2^+ and C_2D_2 greatly exceeds the reaction endoergicity is an additional strong indication that the C_2D fragment acts as a spectator in the abstraction process, and only the energy of O_2^+ relative to the abstracted atom is effective in removing the deuterium atom. Our results also make it clear that spectator stripping can occur in an endothermic reaction process, and is therefore not necessarily to be associated only with "attractive" or "downhill" potential energy surfaces that are thought to occur in exoergic ion-molecule reactions.

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Figure Captions

Fig. 1. Contour maps of the specific intensity of O_2D^+ from the O_2^+ - C_2D_2 reaction at 125 and 99.4eV laboratory energy. The small crosses locate the velocity of O_2D^+ formed by the spectator stripping process. The circles marked Q = -2.3 and Q = -10eV are, respectively, the velocity limits for products with the minimum and maximum allowable internal excitation. The angles are measured in the barycentric system.

Fig. 2. A plot of the relative differential reaction cross section at zero scattering angle as a function of the O_2^+ projectile energy. The upper scales give the energy of the projectile relative to C_2D_2 and relative to the abstracted deuterium atom. The arrow locates the threshold for reaction calculated using the spectator stripping model.

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Table I

E_o[a]	E_r	E_a	V/V_o	Q	$I(\theta=0)$[b]
45.2	21.1	2.66	0.923	-5.5	0.6
50.2	23.4	2.95	0.912	-5.7	2.0
50.7	23.6	2.98	0.914	-5.6	0.9
60.8	28.4	3.58	0.923	-5.5	1.9
61.2	28.5	3.60	0.923	-5.5	1.9
75.1	35.1	4.42	0.933	-5.5	5.2
99.4	46.4	5.84	0.943	-5.5	1.9
100	46.8	5.90	0.942	-5.7	3.3
121	56.4	7.11	0.945	-6.0	2.0
125	58.3	7.35	0.945	-6.1	1.2
140	65.2	8.22	0.949	-6.0	1.1

a. All energies in eV.

b. Arbitrary units.

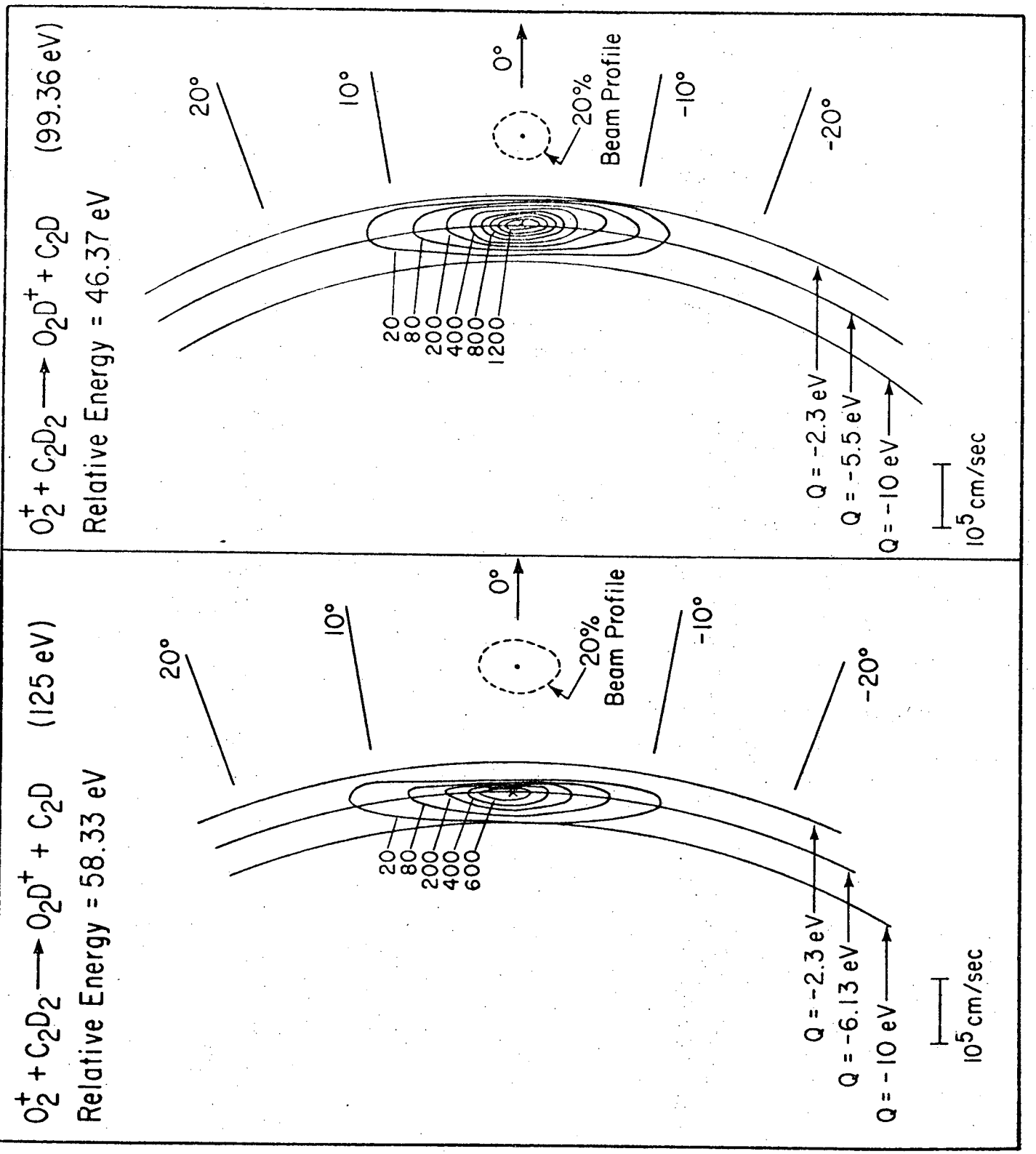

Fig. 1

XRI 721-5967

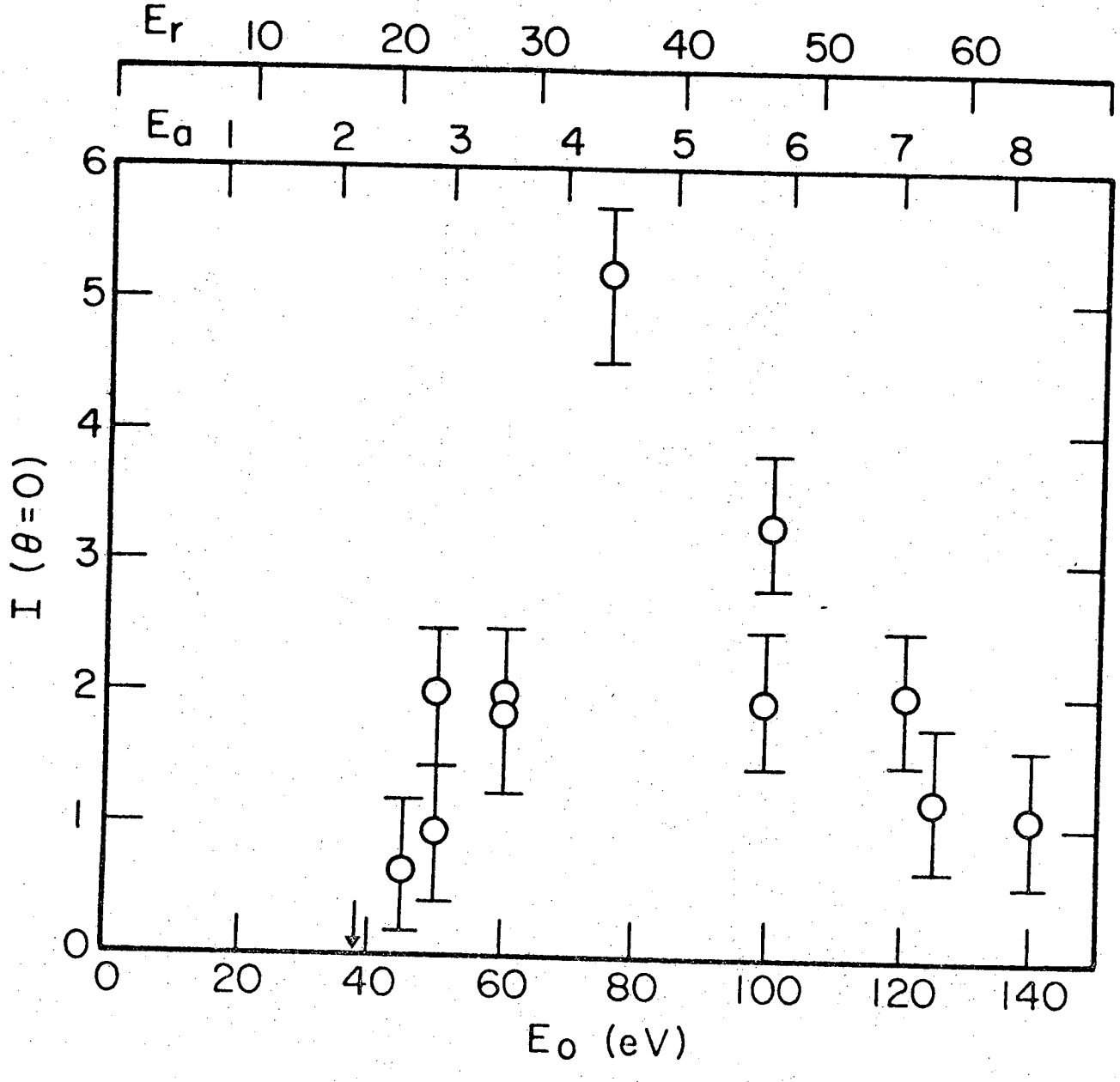

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Fig. 2

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